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The correlation between elongation at break and thermal decomposition of aged EPDM cable polymer

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ABSTRACT

The effect of simultaneous thermal and gamma irradiation ageing on the mechanical and physicochemical properties of industrial EPDM was investigated. Accelerated ageing, covering a wide range of dose rates, doses and temperatures, was preformed in stagnant air on EPDM polymer samples extracted from the cables in use in the Belgian nuclear power plants. The mechanical properties, ultimate tensile stress and elongation at break, are found to exhibit the strong dependence on the dose, ageing temperature and dose rate. The thermal decomposition of aged polymer is observed to be the dose dependent when thermogravimetry test is performed under air atmosphere. No dose dependence is observed when thermal decomposition is performed under nitrogen atmosphere. The thermal decomposition rates are found to fully mimic the reduction of elongation at break for all dose rates and ageing temperatures. This effect is argued to be the result of thermal and radiation mediated oxidation degradation process.

1. Introduction

The lifetime extension of existing Nuclear Power Plant (NPP) relies on the long term stability of a variety of its components. Among those, some of the most important are the power and instrumentation (control) cables. In Belgium, recent decision to continue the operation of oldest reactors has intensified the research related to the cable ageing, in order to support the long term operation of NPPs. The demonstration of the cable functionality for the long term operation requires accelerated cable ageing experiments, which are often focusing on the cable insulation since the loss of insulation properties might lead to the loss of cable functionalities. Some cables used in Belgian NPPs are made of ethylene-propylene-diene monomer (EPDM terpolymer) mixed with additives and slightly cross-linked, in order to improve their mechanical and physical properties (Willan, 2011; Zuidema et al., 2011; Mead et al., 2002).

The use of accelerated ageing experiments for NPP cable evaluation requires the proper extrapolation to NPP relevant conditions. For that purpose, the full understanding of the physical and chemical aspects of ageing, and their correlation with the mechanical properties is of prime importance. Accelerated ageing of the polymers in the oxidizing environment may introduce the dose rate effect which originates from the diffusion-limited polymer oxidation. This effect involves the heterogeneous polymer oxidation, causing the complex interplay of the polymer degradation processes. Two main degradation mechanisms which occur in the EPDM polymers under γ-irradiation and elevated temperatures are the cross-linking and chain scission (Rivaton et al., 2004, 2005a, 2005b). These two processes can occur simultaneously, and their mutual contribution to the polymer degradation depends mainly on an initial degree of cross-linking, the presence of unsaturated chains (double bonds) and the oxidation conditions. The chain scission is stabilized in the oxidizing environment, since alkyl radicals created by γ-irradiation strongly react with the oxygen. The chain scission is thus particularly important at elevated temperatures which facilitates the oxygen diffusion and increases the reactivity of free radicals (Rivaton et al., 2005b; Planes et al., 2010). However, the dose rate variations could also create different oxidation rates. For example, at high dose rates the oxidation could be limited to near surface region, in particular for the short ageing times (low dose). Due to fast creation of the radicals throughout the polymer by γ-irradiation reaction, the high oxygen consumption at the sample surface hinders the oxygen diffusion toward the bulk of the sample. As a consequence, the polymer might oxidize less at high dose rates for the same total dose (Gueguen et al., 1994; Pinel and Boutaud, 1999, 1994), enabling in fact the cross-linking. Because of this effect, an extrapolation method of using the accelerated ageing results for real NPP conditions is still

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the debating subject.

The influence of radiation and thermally mediated oxidation to the polymer degradation were studied by utilizing a variety of techniques. With respect of the mechanical properties, for the ageing at high dose rates, the elongation at break is observed to decrease with increasing the dose, while the ultimate tensile stress remains constant (Clough and Gillen, 1985). On the contrary, at low dose rates the elongation at break retains the high values, while the ultimate tensile strength decreases rapidly by increasing the dose. Seguchi et al. found for the cross-linked polyethylene that the elongation at break and ultimate tensile strength at a given dose are dependent on the dose rate in a way that the change is enhanced at low dose rates (Seguchi and Arakawa, 1981). In the cross-linked ethylene-propylene-rubber, this effect was observed to be less pronounced for elongation at break. Differences in the mechanical properties were described as originating from heterogenous oxidation degradation (Clough and Gillen, 1985; Seguchi and Arakawa, 1981), which influences the interplay of cross-linking and chain scission processes. The effect of heterogeneous oxidation has been fully confirmed by the cross-sectional sample analysis by various techniques such as hardness, density, gel fraction, optical measurements (Clough and Gillen, 1985; Seguchi and Hashimoto, 1981). For the same purpose, Seguchi and Hashimoto (1981) used the chemical techniques in order to determine the oxygen diffusion coefficient and solubility constant. The oxygen consumption and uptake rates were obtained by measuring the differences in pressure during and after ageing process (Zaharescu, 1998).

The mechanical properties that could originate from the heterogeneous oxidation were recently observed in industrial EPDM (S˘arac et al., 2016). In the present study, the previous analysis is extended by performing the mechanical tests on additional samples, as well as by performing the physicochemical analysis, namely the thermogravimetry (TGA) test. Despite the fact that a lot of studies of polymer degradation kinetics have been already carried out by using the TGA (Abadir, 2013; Pistor et al., 2011; Gamlin et al., 2000, 2001), not much work has been reported for the thermal and irradiation aged EPDM polymers. The same samples were used for both the mechanical tests and thermogravimetry measurements. The thermal decomposition processes were analyzed on the basis of radiation and thermally mediated oxidation process, and the correlation between the decomposition rates and elongation at break is established.

2. Materials and methods

The samples used in this study were extracted from the cables installed in Belgian NPPs. The main polymer component in the EPDM, is Nordel 2722 with a norbornadiene as a diene. It's part in the EPDM is 38.1 weight percent (wt%). This cable also contains ethylene vinyl acetate (EVA) polymer (9.5%), that has 50% of vinyl acetate (VA). A high quantity of aluminium hydroxide (ATH) is present (48 wt%) and it is used as a fire retardant filler. The crystallinity of samples is measured with the differential scanning calorimetry (DSC), and it was found to be 0.7 weight percentages. Šarac et al. (2016). The low crystallinity is expected because of the high amount of filler that prevents the arrangement of polyethylenic unites into the crystalline zones. The high amount of VA in EVA inhibits the creation of crystalline zones.

Simultaneous thermal and irradiation ageing is performed at Belgian research center SCK·CEN. The irradiation is performed in the RITA and BRIGITTE irradiation facilities described previously in Fernandez et al. (2002). The RITA facility comprises four 20 cm high cylindrical Co^{60} sources located at ~6.5 m below the water surface. The size of the square formed by the Co^{60} sources can be changed to adjust the dose-rate. The BRIGITTE facility is similar to the RITA with a difference which is reflected in the way the dose-rate adjustment is made. Namely, the BRIGITTE comprises up to 10 Co^{60} sources so the dose-rate is adjust by changing the number of sources. In both facilities the gamma-sources have a length shorter than the sample container height. As a result, the dose-rate inside the container has a vertical gradient with a flat dose-rate area around the mid-plane. A desirable dose-rate can be obtained by changing the vertical position in the irradiation container. The actual dose-rate at the sample location was mapped before the irradiation using Harwell Red Perpex dosimeters. The standard accuracy of the dosimetry is 5.5%. The non-uniformity of the dose-rate distribution over the samples was less than 5% Šarac et al. (2016).

During irradiation the samples were placed in a dedicated cylindrical furnace placed inside the irradiation container to allow accurate temperature control. The temperature was maintained using a PID controller. Stabilization at desired temperature was achieved within ± 0.1 °C.

The volume of this furnace was ~20 l. There was no air supply to the furnace: the irradiation was performed in stagnant air with the air pressure of about 1.3 bar. Typically, 10 samples with the total mass of about 10 g are used for one irradiation condition. Since the EPDM oxygen consumption is about 6.24×10^{-5} mol/g at 10 kGy (Arakawa, 1987), the total oxygen consumption by the samples during irradiation for doses up to 1000 kGy could be up to the 30% of the total volume. Similarly, the critical sample thickness relevant for oxygen limited diffusion is estimated on the basis of IEC report 61244-1 (IEC, 2014) to be in the range between 0.5 and 3 mm, depending on irradiation condition (dose rate and temperature). Contrary to our previous analysis (Šarac et al., 2016), since the sample thickness is about 2 mm, our irradiation conditions are most probably performed with limited oxygen diffusion, causing heterogeneous oxidation.

The ageing matrix is given in Table 1. The ageing temperature was in a range of 25–85 °C, and the dose rate is varied between 106 Gy/h to 2760 Gy/h.

The tensile test was done on the Lloyd LR10K machine, at a speed of 10 mm/min at room temperature (22 °C). The samples were clamped at 8 mm from each side and the crosshead displacement was measured. The displacement was additionally recorded by high resolution digital camera (Šarac et al., 2016).

The TGA test provides the measurements of the sample mass loss as a function of the temperature and time, while the sample is heated in the controlled environment. The TGA was done with the METTLER TOLEDO TGA/SDTA 851e machine in both nitrogen and air (air flow was 50 ml/min), at a constant heating rate of 20 °C/min in a temperature range between 30 and 500 °C. The starting weight of the samples was about 10–15 mg, and the mass loss is presented in the percentages.

3. Results and discussions

The ultimate tensile stress, and the elongation at break of performed mechanical tests, are presented in Figs. 1 and 2. By

Table 1
Ageing matrix of the EPDM samples.

Dose rate Gy/h	Absorbed dose kGy	Ageing temperature °C
250	100 200 300 400 500 600	25
720	200 300 400 500 600 700 800 900 1000 1100	25
1390	200 300 400 600 800 1000	40
2760	317 466 793 1189 1586 2379	40
106	20 40 60 100 200 250	55
455	80 160 240 400 800 1000	55
106	20 40 60 100 200 250	70
455	80 160 240 400 800 1000	70
1390	200 300 400 600 800 1000	70
2760	320 470 800 1200 1600 2400	70
106	20 40 60 100 200 250	85
455	80 160 240 400 800 1000	85